Abstract

Nanostructured ceramics and composites for refractory applications in coal gasification

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Objective

The class of ceramics typified by $NaZr_2(PO_4)_3$ ("NZP") are thermally stable to 1500°C (2700°F) while exhibiting low to zero coefficients of thermal expansion (CTE's) up to 1000°C (~1800°F) or more. Low CTE values confer thermal shock resistance to NZP ceramics. Further, NZP-based ceramics and composites exhibit very low thermal conductivities and some compositions appear to have catalytic properties which promote the oxidation of hydrocarbons. This combination of properties makes NZP-based ceramics particularly attractive for applications requiring thermal management, thermal shock resistance, exposure to aggressive gaseous environments, and gas clean up.

The objective is to prepare monolithic NZP-type ceramics in ways which make them attractive for use in refractory applications, in hot gas separation technologies by controlling their compositions and porosities at the atomic level. An objective is to use casting because, although a bench-level study is being carried out, it is anticipated that the preparative processes used will be amenable to scale-up. Castability is believed provide an economical route to the production of complex, and near net shapes as, for example, in the formation of candle filters.

Accomplishments to Date

In the first phase of the program the mechanistic paths to NZP formation were determined. Specific emphasis was placed on identifying preparative routes which led directly to the formation of NZP with forming intermediates. A second objective was to explore the effect of epitaxy on NZP formation and on the microstructures which develop.

Two compositions were explored, each having unique processing routes that impart to them their own unique properties. The first is the NZP ceramic having composition $NaZr_2(PO_4)_3$. The second is a silicon substituted NZP ceramic having composition $Na_3Zr_2(Si_2P)O_{12}$. Both were made to possess large amounts of porosity suitable for hot gas filtering applications.

For the NZP ceramic having composition $NaZr_2(PO_4)_3$, two types of additives were used: (1) HAp and (2) CuO. Precipitated hydroxyapatite constitutes needles but was dissolved into the NZP structure during firing altering the pore morphology of the resulting ceramic. CuO additions stimulated densification during firing imparting greater strength to the ceramic, though at the expense of internal surface area. The fine pore structure measures about 50 nm and less and contributes approximately 30m^2/g of internal surface area to the fired ceramic component. The addition of HAp coarsens the pore structure and reduces the internal surface area. The pore

size is approximately 0.1 μm when the HAp was added. Further additions of HAp decrease internal surface area but do not contribute to densification.

CuO additions were shown to both further increase the amount of shrinkage the pellets undergo during firing as well as further coarsen the microstructure. Larger grains and grain boundaries were evidence that densification has occurred resulting in higher strengths, but low internal surface area.

Nasicon (Na Super Ionic Conductor) has the composition $Na_3Zr_2(Si_2P)O_{12}$ and is noted for its ionic conductivity. However, the synthesis routes established for this compound rendered the resulting ceramic porous with its own unique microstructure. Two different routes in making porous Nasicon were explored. The first started with a precipitated gel to which amorphous silica was added. The slurry was dried, calcined, milled and pressed into pellets that were fired at 1100^{o}C for 5 hours. The resulting ceramic was observed to expand substantially during firing. This expansion was greater at higher calcination temperatures. The second route entailed not adding the silica until *after* the gel was calcined, which resulted in the ceramic shrinking during firing. This shrinkage was greater at high calcinations temperatures.

The reticulated microstructures of these Nasicon ceramics constituted a flowering of well-developed crystals (1-5 μm) that formed clusters. These clusters were connected in a way to form 3-dimmensionally interconnected structures that left a network of empty spaces ranging in size from 5 to 50 μm.

Future Work

A third objective is to explore the formation of nanostructured NZP matrix composites. A final objective of the program will be to determine various properties including specific surface area, porosity, mechanical properties and ionic conductivities.

Papers

J.V. Bothe and P.W. Brown, "Formation of Nasicon Ceramics with Tailored Microstructures," *Journal of the American Ceramic Society*, submitted.

J.V. Bothe and P.W. Brown, "Low Temerature Synthesis of Porous NZP Ceramics," *Journal of Materials Science*, submitted.

Students Supported

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